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In-Situ Optical Photorefectance During MOCVD LDRD Project 3531040000

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In-Situ Optical Photoreflectance During MOCVD

LDRD Project 3531040000

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Abstract

This report summarizes the development of *in situ* optical photoreflectance as a tool for measuring impurity concentrations in compound semiconductors. We have successfully explored the use of photoreflectance as an *in situ* tool for measuring n-type doping levels in metal-organic chemical vapor deposition (MOCVD) grown GaAs materials. The technique measures phase and frequency shifts in Franz-Keldysh oscillations measured on uniformly doped thin films. Doping concentrations from 5×10^{16} to 1×10^{18} can be measured at temperatures below 130 C. A method has been developed to include photoreflectance as the last step in our pre-growth *in situ* calibration procedure for MOCVD thin film structures. This combined capability now enables us to rapidly and accurately determine growth rates, chemical composition, and doping levels necessary to generate a recipe to fabricate complex optoelectronic compound semiconductor devices.

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INTRODUCTION

This report summarizes the development of *in situ* optical photoreflectance as a tool for measuring impurity concentrations in compound semiconductors. The goal of this program was to use photoreflectance during the growth of compound semiconductors to extract the concentration of intentionally doped impurities in device structures.

Over the past three years, Sandia has invested in the development of normal-incidence optical reflectance monitoring and analysis techniques and in their integration into our MOCVD (metal-organic chemical-vapor deposition) and molecular beam epitaxy (MBE) tools. The result has been an agile and efficient materials growth capability. This capability has been a major contributor to Sandia's ongoing successes in compound-semiconductor devices (e.g., VCSELs).

Despite its successes, however, normal-incidence optical reflectance is inherently limited to measuring gross structural (e.g., composition and thickness) rather than subtler electronic (e.g., carrier concentrations and profiles) properties. Because these electronic properties are a key determinant of device performance, this limitation is a major roadblock to an integrated, "process-to-performance" capability in compound-semiconductor device prototyping. In this project, we proposed to address this limitation by exploring the development of normal-incidence optical photoreflectance in a MOCVD tool.

Optical photoreflectance (PR) is a technique in which one measures changes in optical reflectance caused by electron-hole pairs photo-induced by a second, modulated optical beam. Because it is a differential technique, it can be exceedingly sensitive. Moreover, because of interactions between the electron-hole pairs and internal electric fields, the technique is also exceedingly sensitive to the details of band offsets, Fermi levels, and overall band-gap engineering present in the growing heterostructure. As a consequence, the technique would enable, for the first time, *in situ* measurements of true electronic properties.

As one example, in the intermediate modulation field regime, photon-assisted transitions in the presence of built-in electric fields are known to give rise to so-called Franz-Keldysh oscillations. These oscillations depend on electric field strengths which, in undoped layers, depend in turn on Fermi energies and carrier concentrations in doped claddings. They can, therefore, be used to extract carrier (and doping) concentrations, a long sought-after "holy grail" of *in situ* monitoring research.

We also expect optical photoreflectance to be a powerful new tool not only for improving MOCVD technology and application, but also for enhancing our understanding of MOCVD science. For example, real-time measurements of dopant incorporation can be expected to enhance understanding of dopant chemistry and segregation, a difficult area ripe for major advances. Real-time measurements of surface band-bending can be expected to enhance understanding of adsorption-induced changes in surface electronic structure.

EXPERIMENT

A schematic diagram of the photorefectance (PR) apparatus is shown in Fig. 1. Monochromatic light from a tungsten-halogen source is sent through a 0.6 mm single-core optical fiber to a beamsplitter assembly located above the wafer sample. Normal incidence reflectance from the sample is detected by a silicon photodiode and transimpedance amplifier. Two signals are recorded. The first is the DC reflectance of the wafer, R . The second is the modulated change in reflectance induced by a 40 Hz chopped HeNe laser, ΔR . A DSP lock-in amplifier is used to detect these signals and to output the ratio, $\Delta R/R$. The $\Delta R/R$ signal is stored in a computer as the monochromator wavelength is scanned over the bandgap region of the sample. Because PR signals are sensitive to the total light flux on the sample, neutral density filters were used to obtain the least distorted signals. The apparatus dimensions were chosen to simulate an in situ implementation of this experiment on the EMCORE 3200 MOCVD reactor. The wafer was mounted on a hot plate to record PR spectra at elevated temperatures.

Fig. 1: Schematic of the apparatus used to perform the photorefectance experiments.

RESULTS

Fig. 2 shows photorefectance spectra for five samples with a layer structure designed to enhance Franz-Keldysh oscillations (FKO's). All samples consisted of a 5000 Å doped layer

overlaid with a 1000 Å unintentionally doped “cap” layer. This structure creates a large, relatively uniform electric field across the cap layer. The frequency of the FKO’s is inversely proportional to the electric field established in the cap layer. Beat patterns seen in the oscillations are due to heavy-hole and light-hole contributions manifested through their different effective masses. A small disturbance is seen at the spin-orbit critical point near 1.9 eV, but the largest contribution to the photorefectance signal is from the bandgap region. Fig. 2 clearly shows a doping level dependence that results in a monotonic decrease in the FKO frequency as the doping level increases. Other features show up in this figure which are not understood, such as the phase shift in oscillation patterns between the lowest level doping and the rest of the curves, and a splitting of the FKO peaks at the highest doping level.

Fig. 2: Photorefectance spectra of five capped-layer structures having 1000 Å of unintentionally doped GaAs on a 5000 Å layer doped n-type to the level indicated in the figure.

There was not enough time in this project to thoroughly analyze the data in Fig. 2, but a cursory analysis indicated that the oscillations corresponded to expected surface electric field strengths at the low doping levels, but the high doping levels yielded smaller than expected electric fields.

It appears that the data in Fig. 2 can provide one with a method for in situ calibration of doping levels. It does, however require growing a special structure to bring out the FKO's. Early in the project, we discovered that simple bulk layers doped n-type also yielded FKO's. Because of this added simplicity, we explored these kind of structures to determine whether they could be exploited for a doping level calibration tool.

Fig. 3 shows photoreflectance spectra of bulk GaAs films doped n-type for a wide range of doping levels. Because the electric field near the sample surface is no longer uniform with depth, the FKO's are damped when compared to the FKO's in Fig. 2. However, there is still a clear trend to longer oscillation periods as a function of doping level. There is also a systematic shift in the overall pattern which adds to the doping level sensitivity.

Fig. 3: Photoreflectance spectra of eight bulk layers doped n-type to the level indicated in the figure. Arrows mark two of the eight second-extremum positions plotted in Fig. 4

Fig. 4 plots the photon energy of the second FKO extremum (marked by arrows in two out of the eight samples in Fig. 3) as a function of doping level. Fig. 4 shows a nearly exponential dependence that could be used as an empirical calibration curve relating the second FKO extremum position to a carrier concentration. The slope of this curve yields a calibration

sensitivity comparable to that of Hall measurements over a wide range of doping levels. Further sensitivity could be gained by using chemometric methods to extract doping levels from the full spectral line shape features of the calibration set.

Fig. 4: Plot of the energy of the second large extremum feature observed in PR (eg. arrows in Fig. 3) as a function of the carrier concentration (concentration measured by the Hall effect).

Experiments were performed at elevated temperatures to explore the use of this technique as a real-time probe of doping level. Unfortunately, the signals were strongly dependent on temperature. The FKO lineshapes were completely washed out above only 130 °C. This method thus is not suitable for high-temperature measurements.

FKO's were observed for capped-layer p-type structures, but no oscillations were observed for bulk p-type doped layers. Also, highly doped bulk n-type layers, eg. 8e18 did not exhibit FKO's.

CONCLUSIONS

Unfortunately, this project was far too limited to thoroughly investigate all the phenomena observed in the experiments. However, it did satisfy its main goal to determine whether an in situ monitor could measure electronic properties such as doping levels. The successful implementation of this kind of probe is so significant that further work is planned to complete the study using other sources of funding.

Even with the preliminary data taken in this study, it is possible to devise a calibration scheme that exploits the relationship shown in Fig. 4. We normally perform a pre-growth calibration run to extract growth rates for a given set of MOCVD reactor conditions. This run typically deposits less than a dozen layers, each roughly 2000 Å thick, of different materials. The growth rate of each layer may be extracted from the in situ reflectance taken during the run. At the end of the calibration sequence, a final 3000 Å thick doped layer could be grown. The sample could then be cooled down to ~100 C where an in situ photoreflectance spectrum could be taken to determine the doping level. Depending on the calibration measurement, conditions could then be adjusted to correct for differences between measured and expected growth rates and doping levels. If necessary, the sample could be heated up again for repeated calibration layers. Although this procedure is less desirable than a real-time in situ monitor, it is still vastly superior to post-deposition measurements of doping level using Hall probes, which are destructive and much more time consuming than a PR scan that takes only a few minutes.

The pre-growth strategy has proven to be a very effective tool for practical synthesis of very complex structures such as VCSEL's. Implementation of a similar strategy for doping level using photoreflectance promises to yield equally effective results.

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